

A New Synthetic Analogue Of The Burckhardtite Mineral, $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$: Synthesis, Structure, And Properties

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The mineral, Burckhardtite, $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$, is synthesized and characterized. A new analogue, $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$, is successfully prepared for the first time under laboratory conditions. The substitution of Ga^{3+} by $\text{Ti}_{0.5}\text{M}_{0.5}$ ($\text{M} = \text{Co}^{2+}, \text{Ni}^{2+}$) results in new compounds with the Burckhardtite mineral structure. The transition metal-containing compounds exhibit interesting new colors, partly resulting from d-d transitions and metal-to-metal charge transfer (MMCT) transition. The Ga compound shows a deep UV cut-off (~86%), which is one of

the better known values of deep UV cut-off compounds. The compounds exhibit good dielectric behavior with low dielectric loss. The Eu^{3+} -substituted samples show deep red emission with a long lifetime of ~0.89 ms. The magnetic behavior of the transition metal containing compounds indicates anti-ferromagnetic interactions. The successful synthesis of the naturally occurring mineral along with newer analogues with interesting properties suggests that it is profitable to investigate compounds of mineral origin.

1. Introduction

In the realm of inorganic solid-state chemistry, compounds based on oxides are dominant. Generally, compounds based on perovskites, pyrochlore, and spinel structures have been investigated extensively over the years.^[1–7] Minerals and their structures are another class of compounds that have been given limited attention. The naturally occurring minerals are one of the largest family of known compounds, most of which remain unexplored.^[8–11] The issues with regard to mineral and mineral structures are: (i) Difficult to synthesize in pure form under laboratory conditions; and (ii) many mineral structures have a number of elements occupying the same crystallographic position – the exact role of the various elements towards the structural stability is not yet clear. In spite of these difficulties, there have been many studies towards the exploration of compounds based on mineral structures with many different properties.^[12–18]

We have been interested in the study of compounds based on mineral structures during the past decade, which resulted in new colored compounds, multiferroic behavior, white light emissions, and visible light-driven organic transformations.^[19–22] In continuation of this theme, we have now focussed our attention to an aluminosilicate mineral Burckhardtite, $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$.^[23,24]

The structure of Burckhardtite is based on two distinct layers: one made from tetrahedral aluminosilicate $[\text{AlSi}_3\text{O}_8]^-$ layer, and the other octahedral phyllosilicate $[\text{FeTeO}_6]^{3-}$ layer.

The Pb^{2+} ions are located in between the phyllosilicate and phyllosilicate layers. The Burckhardtite structure offers reasonable scope to investigate the tolerance of the structure towards substitution either at the phyllosilicate or the phyllosilicate layers. In addition, the laboratory synthesis of Burckhardtite is not yet known. These prompted us to investigate the synthesis, substitutional study, and their associated properties of the compounds that are based on Burckhardtite structure. As part of this study, we were able to synthesize a new analogue of the Burckhardtite structure by substituting the Fe^{3+} ions by Ga^{3+} ions, which formed $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$. In this paper, the synthesis, structure, dielectric, magnetic, and optical behavior of the compounds with the Burckhardtite structure is presented.

2. Results and Discussion

The PXRD pattern of the laboratory synthesised compound, $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ along with the newly prepared $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ and the other substituted compounds indicated phase purity (Figure 1; ESI Figure S1, Table S1). The PXRD patterns of the compounds were compared with the simulated pattern of the $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ phase, which is based on the structure reported earlier.^[23,24]

The newly synthesized gallium-containing compound, $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ was refined using the $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ structure as the model. The Rietveld refinement of both the known $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ as well as the $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ phases were carried out by the GSAS Expgui program (Figure 2). The refinement of the parent $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ phase suggests a good fit to the reported structure (ESI Figure S2; Table S2).^[23] The substitution of the Ga^{3+} ions in place of the Fe^{3+} ions exhibited changes in the lattice parameter as well as the cell volume. While the a and b lattice parameters exhibited a decrease, the c lattice parameter indicated an increase on substituting the Ga^{3+} ions in place of the Fe^{3+} ions. We observed a slight reduction in the volume for the Ga^{3+} ions

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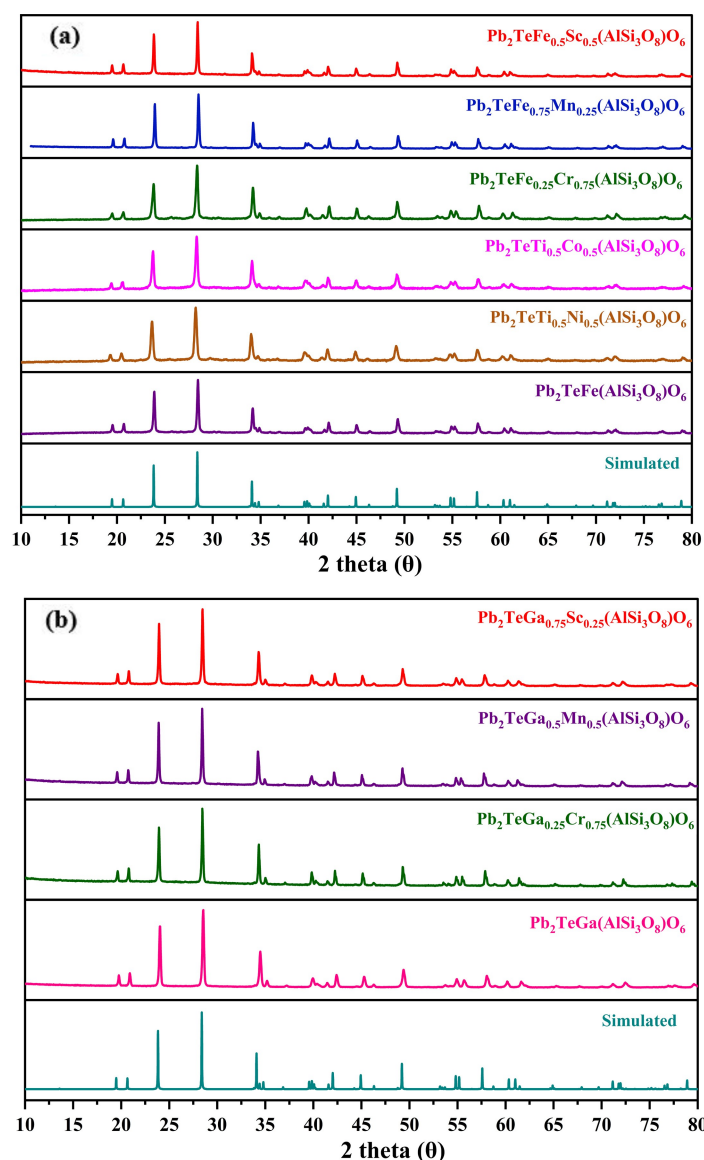


Figure 1. Experimental PXRD patterns of the prepared compounds (a) Substitution at the Fe^{3+} site (b) Substitution at the Ga^{3+} site

substituted compound ($308.8(8) \text{ \AA}$) compared to the parent Fe^{3+} ions containing compound ($311.2(1) \text{ \AA}$). The refinement of the $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ phase indicated an excellent fit to the

structural model of $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compound, which incidentally suggests that the Ga^{3+} ions completely replace the Fe^{3+} ions in the structure (Figure 2; Table 1).

Table 1. Crystallographic data of $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ from the Rietveld refinement data.

S.No.	Element	x	y	z	Occ.	U	Site
1	Pb	1	0	0.3173	1	0.020	2e
2	Te	2/3	1/3	1/2	0.5	0.027	2d
3	Ga	2/3	1/3	1/2	0.5	0.027	2d
4	Si	1/3	2/3	0.1247	0.75	0	4h
5	Al	1/3	2/3	0.1247	0.25	0	4h
6	O1	1/3	2/3	0	1	0.014	2c
7	O2	0.4543	0	0.1669	1	0.022	6k
8	O3	0.6308	0	0.4177	1	0.006	6k

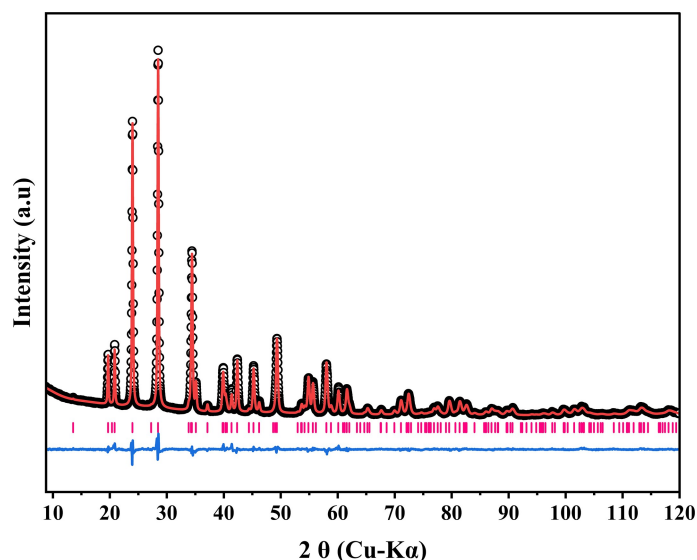


Figure 2. Rietveld Refinement of $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$. The observed (O), the calculated (Red line), and the difference (bottom blue line) are shown. The vertical bars (|) indicate the Bragg's reflections.

Space group $P-31m$; $a=b=5.2173(1)\text{\AA}$; $c=13.1029(9)\text{\AA}$; $V=308.883\text{\AA}^3$; $\alpha=\beta=90^\circ$; $\gamma=120^\circ$; Reliability factors: $R_p=2.5\%$; $R_{wp}=3.3\%$; $\chi^2=4.52$; average bond lengths [$\text{\AA}$]: $\text{Te/Ga-O}=1.973(9)$; $\text{Si/Al-O}=1.625(2)$; $\text{Pb-O}=2.958(8)$. Structural model is taken from Ref:[23].

The crystal structure of $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ is shown in Figure 3. The structure is same as that of the parent burckhardtite compound, $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$. As mentioned before, the tetrahedral phyllosilicate bi-layers are separated by the octahedral phyllosilicate bi-layers by the Pb^{2+} ions. The Pb^{2+} ions are 9-coordinated (ESI, Figure S6). The interesting aspect of the Burckhardtite structure is the presence of two types of bilayer: (i) the aluminosilicate tetrahedral bilayer ($[\text{AlSi}_3\text{O}_8]^-$), and (ii) the bi-octahedral layer ($[\text{GaTeO}_6]^{3-}$). The differences in the ionic sizes between the Te^{6+} ($0.56\text{\AA}$) and Ga^{3+} ions ($0.62\text{\AA}$) as well as separation between them favors ordering in the structure. Similar behavior was also observed in $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compound as well.^[23]

3. X-Ray Photoelectron Spectroscopic (XPS) Studies

We carried out the X-ray photoelectron spectroscopic (XPS) studies on the those compounds containing transition elements to learn about their oxidation states. Thus, we examined $\text{Pb}_2\text{TeTi}_{0.5}\text{Co}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeTi}_{0.5}\text{Ni}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeFe}_{0.75}\text{Mn}_{0.25}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeGa}_{0.5}\text{Mn}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeFe}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$, and $\text{Pb}_2\text{TeGa}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compounds (Figure 4; ESI Figure S7). The Co^{2+} ions in $\text{Pb}_2\text{TeTi}_{0.5}\text{Co}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$ exhibited two main peaks at $\sim 780.6\text{ eV}$ and $\sim 796.2\text{ eV}$, which can be assigned to the $2p_{3/2}$ and $2p_{1/2}$ binding energies of Co^{2+} ions.^[25] The satellite peaks observed at $\sim 786.5\text{ eV}$ and $\sim 802.8\text{ eV}$ have a value of 6 eV higher than the

main $2p_{3/2}$ binding energy ($\sim 780.6\text{ eV}$) suggests the presence of octahedrally coordinated Co^{2+} ions.^[26] The energy separation between the $2p_{3/2}$ and $2p_{1/2}$ is $\sim 15.5\text{ eV}$ which also suggests the presence of Co^{2+} ions in octahedral coordination. Similar features have been observed before.^[26,27]

The XPS spectra of the Ni^{2+} ions in the $\text{Pb}_2\text{TeTi}_{0.5}\text{Ni}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, also exhibited two main peaks at $\sim 855.8\text{ eV}$ and $\sim 874.03\text{ eV}$ which can be assigned to the $2p_{3/2}$ and $2p_{1/2}$ binding energies of Ni^{2+} ions. An intense satellite peak at $\sim 861.9\text{ eV}$ along with a weak satellite peak at $\sim 878.8\text{ eV}$ is also observed. The separation between the binding energies of $2p_{3/2}$ and $2p_{1/2}$ was observed to be 18.5 eV . Similar values have been observed before for octahedrally coordinated Ni^{2+} ions.^[28,29]

The XPS spectra of Mn^{3+} ions in the $\text{Pb}_2\text{TeGa}_{0.5}\text{Mn}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, and $\text{Pb}_2\text{TeFe}_{0.75}\text{Mn}_{0.25}[\text{AlSi}_3\text{O}_8]\text{O}_6$ exhibited two main peaks. The peaks at $\sim 644\text{ eV}$ and $\sim 653.8\text{ eV}$ for $\text{Pb}_2\text{TeGa}_{0.5}\text{Mn}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$ could be due to the $2p_{3/2}$ and $2p_{1/2}$, respectively and the splitting between the two states is $\sim 9.8\text{ eV}$. For $\text{Pb}_2\text{TeFe}_{0.75}\text{Mn}_{0.25}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compound the peaks were observed at $\sim 644.9\text{ eV}$ and $\sim 653.6\text{ eV}$, which again corresponds to $2p_{3/2}$ and $2p_{1/2}$, respectively. Here, the separation between the two spin-orbit states is 8.8 eV . These are typical values and similar values have been observed for the Mn^{3+} ions in the octahedral coordination.^[30,31]

For the Cr^{3+} ions in $\text{Pb}_2\text{TeGa}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$, we observed two peaks at $\sim 576.6\text{ eV}$ and $\sim 586.9\text{ eV}$, which could be due to the $2p_{3/2}$ and $2p_{1/2}$ binding energies. The separation between the two binding energies was observed as 10.36 eV . Similar behavior was also observed for Cr^{3+} ions in $\text{Pb}_2\text{TeFe}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$ (ESI, Figure S7).^[32] The XPS spectra for other compounds we also found to be in expected range (Table 2)

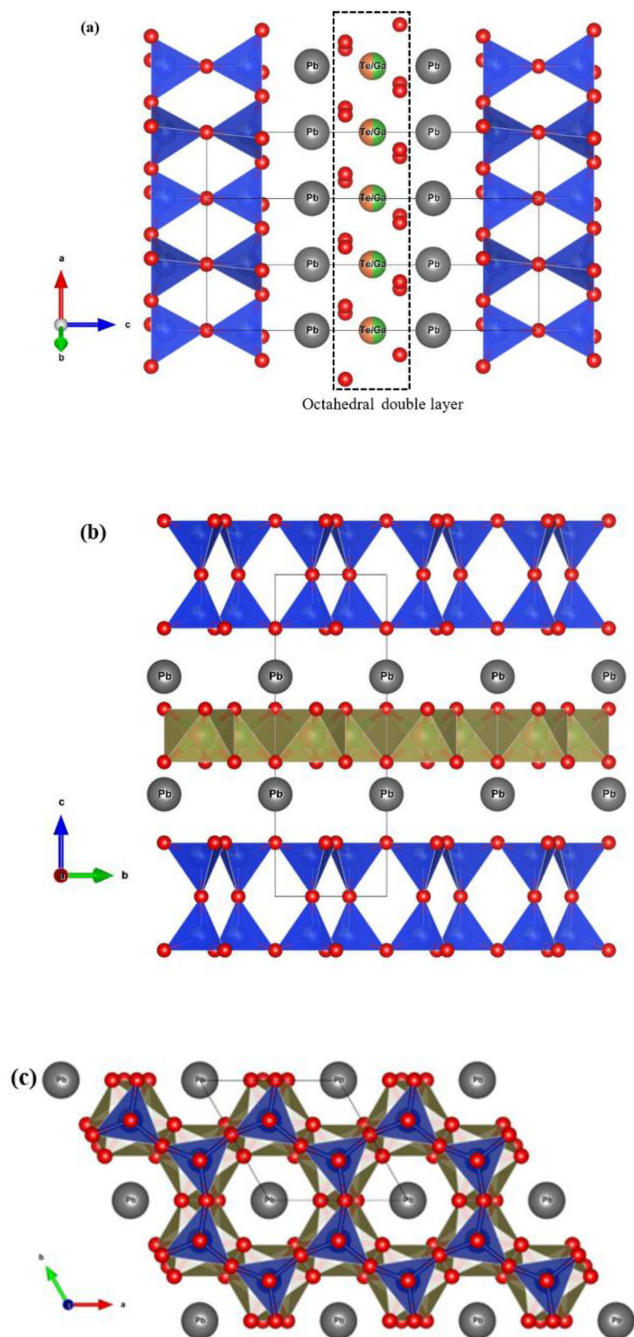


Figure 3. Crystal structure of $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$: (a) viewed shows the tetrahedral $[\text{AlSi}_3\text{O}_8]^{3-}$ double layer along with the octahedral $[\text{TeGaO}_6]^{3-}$ layers, (b) the view along 'bc' plane, and (c) the view along 'ab' plane.

4. Raman Spectroscopic Studies

The Raman spectroscopic studies were carried out on the $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ and its substituted analogs in the range of $50\text{--}1200\text{ cm}^{-1}$ (Figure 5; Figure S8). The compound exhibits strong bands at 689 cm^{-1} and 640 cm^{-1} , which may be due to the Te–O (TeO_6) symmetric stretching vibration (ν_1). The medium-intensity band observed at 475 cm^{-1} could be due to the Te–O bending mode (ν_4).^[36] A weak band at 832 cm^{-1} can be attributed to the stretching of the aluminosilicate moiety.

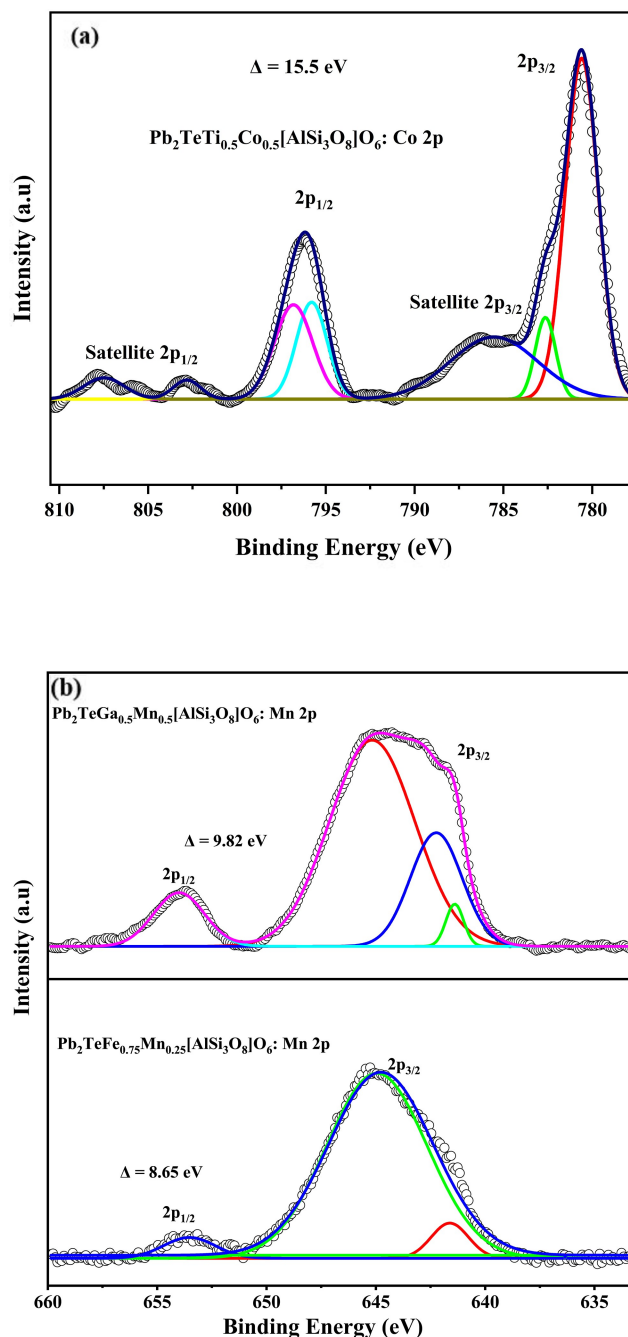


Figure 4. XPS Studies of (a) Co 2p in $\text{Pb}_2\text{TeTi}_{0.5}\text{Co}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, and (b) Mn 2p in $\text{Pb}_2\text{TeGa}_{0.5}\text{Mn}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, and $\text{Pb}_2\text{TeFe}_{0.75}\text{Mn}_{0.25}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compounds.

The bands observed below 560 cm^{-1} (108 cm^{-1} , 139 cm^{-1} , 197 cm^{-1} , 237 cm^{-1} , 292 cm^{-1} , 320 cm^{-1} , 388 cm^{-1} , 475 cm^{-1} , and 554 cm^{-1}) could be due to the bending vibrations of the $[\text{AlSi}_3\text{O}_8]^{3-}$ and $[\text{TeFeO}_6]^{3-}$ units.^[23] The substitution of ($\text{Ti}_{0.5}\text{Co}_{0.5}$) and ($\text{Ti}_{0.5}\text{Ni}_{0.5}$) in place of Fe^{3+} gives rise to changes in the Raman spectra. A strong band observed for both the compounds at 704 cm^{-1} along with a shoulder at 667 cm^{-1} , could be due to the O–Ti–O stretching of the TiO_6 octahedra.^[37] These Raman bands also coincides with the stretching bands of the TeO_6 octahedra, which results in a broader band. The important observed Raman bands are listed in Table S5 (ESI).

Table 2. The summary of XPS spectra of the compounds.

S.No	Compound	B.E. ₍₁₎ ^a (eV)	B.E. ₍₂₎ ^b (eV)	Energy Separation (eV)	Ox. state	Ref.
1	Pb ₂ TeTi _{0.5} Co _{0.5} [AlSi ₃ O ₈]O ₆ : Te 3d	576.2	586.6	10.4	6	[33]
2	Pb ₂ TeTi _{0.5} Co _{0.5} [AlSi ₃ O ₈]O ₆ : Ti 2p	458.2	464	5.8	4	[34]
3	Pb ₂ TeTi _{0.5} Ni _{0.5} [AlSi ₃ O ₈]O ₆ : Te 3d	576.7	587	10.3	6	[33]
4	Pb ₂ TeTi _{0.5} Ni _{0.5} [AlSi ₃ O ₈]O ₆ : Ti 2p	458.7	464.4	5.7	4	[34]
5	Pb ₂ TeFe _{0.75} Mn _{0.25} [AlSi ₃ O ₈]O ₆ : Te 3d	576.5	586.9	10.4	6	[33]
6	Pb ₂ TeFe _{0.75} Mn _{0.25} [AlSi ₃ O ₈]O ₆ : Fe 2p	711.3	725.1	13.8	3	[35]
7	Pb ₂ TeGa _{0.5} Mn _{0.5} [AlSi ₃ O ₈]O ₆ : Te 3d	576.6	586.9	10.3	6	[33]
7	Pb ₂ TeFe _{0.25} Cr _{0.75} [AlSi ₃ O ₈]O ₆ : Te 3d	576.2	586.6	10.4	6	[33]
8	Pb ₂ TeFe _{0.25} Cr _{0.75} [AlSi ₃ O ₈]O ₆ : Fe 2p	711.4	725.6	14.2	3	[35]
9	Pb ₂ TeGa _{0.25} Cr _{0.75} [AlSi ₃ O ₈]O ₆ : Te 3d	576.6	586.9	10.3	6	[33]

a) represents Binding energy for Te 3d (3d_{3/2}), and Fe 2p (2p_{3/2}); b) represents Binding energy for Te 3d (3d_{5/2}), and Fe 2p (2p_{1/2}).

The substitution of other transition metals such as Cr³⁺, and Mn³⁺ in place of Fe³⁺ did not result in much changes in the Raman bands (Table S5). We have observed a new peak at 826 cm⁻¹ for the Cr³⁺ containing compound, which may be associated with the aluminosilicate group. The higher intensity of the Raman band could be due to the increase in the polarization of the aluminosilicate group due to the introduction of Cr³⁺.^[38]

The newly synthesized Ga - compound, Pb₂TeGa[AlSi₃O₈]O₆, also exhibited Raman bands that are comparable to Pb₂TeFe[AlSi₃O₈]O₆ (Table S5).

5. Ultraviolet-Visible (UV-Vis) Spectroscopic Studies

The parent compound, Pb₂TeFe[AlSi₃O₈]O₆, was found to have a beige color under daylight (ESI, Figure S9). The UV-Vis spectra of the compound exhibited only one absorption band around ~470 nm. The Fe³⁺ ions (d⁵) in the octahedral crystal field exhibit ⁶A_{1g} as the ground state.^[39] The three possible transitions for the Fe³⁺ ions are: (i) ⁶A_{1g}(S)→⁴T_{2g}(G); (ii) ⁶A_{1g}(S)→⁴T_{1g}(G); (iii) ⁶A_{1g}(S)→⁴A_{1g}(G).^[39-41] The observed band at ~470 nm could be due to the ⁶A_{1g}(S)→⁴A_{1g}(G) transition.^[39]

The substitution of (Ti_{0.5}Mn_{0.5}) (M=Co, Ni) in place of Fe³⁺ resulted in compounds having tea green and mint green for Pb₂TeTi_{0.5}Co_{0.5}[AlSi₃O₈]O₆, and Pb₂TeTi_{0.5}Ni_{0.5}[AlSi₃O₈]O₆, respectively. Normally the presence of Co²⁺ ions in the octahedral coordination results in pink/purple color, and Ni²⁺ ions green in color. In the present compounds, we observed colors that are different. The UV-Vis absorption spectra for the Pb₂TeTi_{0.5}Co_{0.5}[AlSi₃O₈]O₆ compound exhibited two absorption bands at ~514 nm, and ~682 nm (Figure 6). The allowed transitions for the Co²⁺ ions in an octahedral coordination environment are (i) ⁴T_{1g}→⁴T_{1g}(P), (ii) ⁴T_{1g}→⁴T_{2g}(F), (iii) ⁴T_{1g}→⁴A_{2g}(F). Of these, the ⁴T_{1g}→⁴T_{2g}(F) transition, normally, is observed in the IR region.^[42] The main observed bands at ~682 nm (1.8 eV) and the weaker absorption at ~514 nm (2.6 eV), could be due to

the ⁴T_{1g}→⁴A_{2g}(F), and ⁴T_{1g}→²A_{1g}(G) transitions, respectively.^[42,43] The ⁴T_{1g}→²A_{1g}(G) transition appears to be weak possibly due to the interaction between the ⁴T_{1g} (P) state and the doublet arising from the ²P and ²G states.^[43,44] In addition, there may be metal-to-metal charge transfer (MMCT) involving the Ti⁴⁺ (3d⁰) ions and Co²⁺ (3d⁷) ions. Such MMCT transitions involving d⁰ and dⁿ states have been observed before.^[45-48] The absorption spectra of Pb₂TeTi_{0.5}Ni_{0.5}[AlSi₃O₈]O₆ indicated a strong absorption at ~664 nm (1.85 eV) and a weaker one at ~796 nm (1.56 eV). The Ni²⁺ ions in octahedral coordination exhibits the following transitions: (i) ³A_{2g}→³T_{1g}(P); (ii) ³A_{2g}→³T_{2g}(F); (iii) ³A_{2g}→³T_{1g}(F). The main absorption at ~1.85 eV and the shoulder at ~1.56 eV are the known transitions for the Ni²⁺ ions in octahedral coordination and correspond to ³A_{2g}→³T_{1g}(F) and ³A_{2g}→¹E_g transitions, respectively.^[49,50]

We have also substituted Mn³⁺ ions in place of Fe³⁺ ions and Ga³⁺ ions in Pb₂TeFe[AlSi₃O₈]O₆, and Pb₂TeGa[AlSi₃O₈]O₆, respectively (ESI, Figure S9). The Mn³⁺ substituted compounds exhibited a pale color under daylight for x=0.25. The observed transitions were at ~474 nm (2.61 eV) and at ~532 nm (2.33 eV). The absorption band at ~532 nm (2.33 eV) may be due to the ⁵E_g to ⁵T_{2g} transition.^[51,52] Under tetragonal Jahn-Teller distortion, ⁵E energy level splits into ⁵E' and ⁵E''.^[52] The weak absorption band at ~474 nm could be from the ⁵E_g to ³T_{1g} (H) transition which is spin-forbidden.^[53] This transition also overlaps with the ⁶A_{1g}(S)→⁴A_{1g}(G) transition of Fe³⁺ ions at ~470 nm. The Mn³⁺ substituted Pb₂TeGa_{1-x}Mn_x[AlSi₃O₈]O₆ (x=0.25,0.5) has a slightly brighter pink color under daylight. The UV-Vis spectra exhibited a strong band at ~532 nm (2.33 eV) along with a weaker shoulder at ~484 nm (2.56 eV). The band at ~532 nm could be due to the ⁵E_g to ⁵T_{2g} transition,^[51,52] and the weaker shoulder at ~484 nm to the spin forbidden ⁵E_g to ³T_{1g} (H) transition.^[53]

Our efforts in substituting Cr³⁺ ions in place of Fe³⁺ ions and Ga³⁺ ions were successful and we substituted up to 0.75 Cr³⁺ ions in place of both Fe³⁺ and Ga³⁺ ions. The color of the Cr³⁺ ions substituted compounds (Fe³⁺ ions) was found to be different shades of green under daylight. Cr³⁺ ions in octahedral crystal field is known to exhibit three transitions: (i) ⁴A_{2g}(F)→⁴T_{2g}(F); (ii) ⁴A_{2g}(F)→⁴T_{1g}(F); (iii) ⁴A_{2g}(F)→⁴T_{1g}(P). The UV-Vis

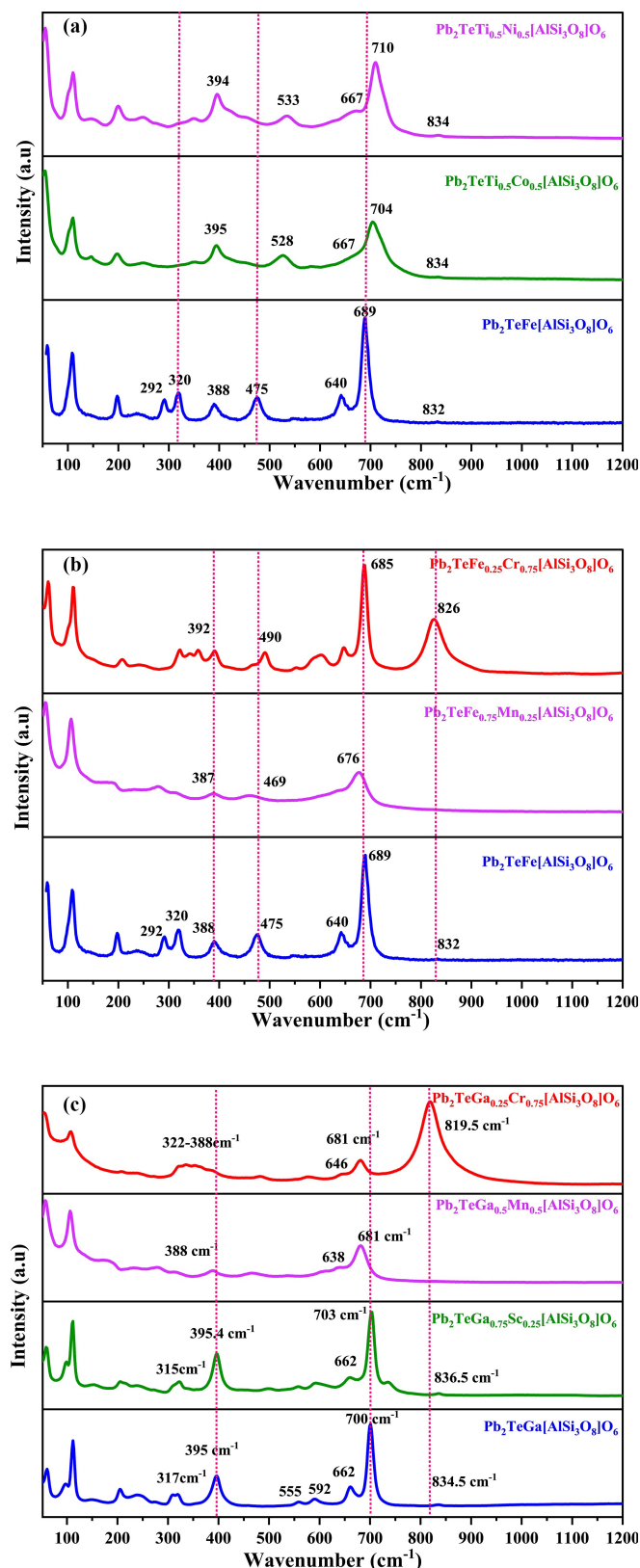


Figure 5. Raman spectra of (a) $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ and $\text{Pb}_2\text{TeTi}_{0.5}\text{M}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$ ($\text{M}=\text{Co}, \text{Ni}$); (b) $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ and $\text{Pb}_2\text{TeFe}_{1-x}\text{M}_x[\text{AlSi}_3\text{O}_8]\text{O}_6$ ($\text{M}=\text{Mn}^{3+}$ ($x=0.25$), Cr^{3+} ($x=0.75$)); (c) $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ and $\text{Pb}_2\text{TeGa}_{1-x}\text{M}_x[\text{AlSi}_3\text{O}_8]\text{O}_6$ ($\text{M}=\text{Mn}^{3+}$ ($x=0.5$), Cr^{3+} ($x=0.75$), and Sc^{3+} ($x=0.25$)).

spectra of Cr^{3+} compound exhibit an absorption at ~ 422 nm and a stronger band at ~ 625 nm, which may be due to the ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$, and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ transitions, respectively (ESI Figure S9).^[54–57] We also observed shoulder bands at ~ 686 nm and at ~ 726 nm. These shoulder bands could be due to the ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^2\text{T}_{1g}(\text{G})$, and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{E}_g(\text{G})$ transitions, respectively.^[55] The substitution of Cr^{3+} ions in place of Ga^{3+} ions exhibited colors that are slightly different from those observed for the Fe^{3+} -containing compounds. The two main absorption bands observed in the UV-Vis spectra for $\text{Pb}_2\text{TeGa}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$ were at ~ 451 nm (2.75 eV), and at ~ 625 nm (1.98 eV), which could be due to the ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$, and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ transitions, respectively.^[54–57] A weak shoulder observed in the UV-Vis spectra at ~ 724 nm (1.71 eV) could be due to the ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{E}_g(\text{G})$ transitions (Figure 6).^[55]

We made estimates of the band gap values employing the Tauc's plot. The parent compound, $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$, has a band gap of ~ 2.68 eV.^[58,59] The band gap was found to increase when Ga^{3+} ions replaces the Fe^{3+} ions in $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ to ~ 3.91 eV (ESI, Figure S10). The lower band gap values observed for the $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ could be due to the s-d and p-d orbital mixing between the Fe^{3+} and O^{2-} orbitals.^[60] Substitution of Cr^{3+} ions in place of Fe^{3+} in $\text{Pb}_2\text{TeFe}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$ reduces the band gap values further to 2.13 eV (ESI, Figure S10). The observed decrease in the band gap values for the Cr^{3+} ions containing compound could be due to the sp-d exchange interactions between the Fe^{3+} (d^5) and the Cr^{3+} (d^3) electrons.^[61] Similar trend was also observed for the Cr^{3+} ions substituted $\text{Pb}_2\text{TeGa}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compound as well. We also noted that the substitution of other transition metal ions in place of Fe^{3+} ions also reduces the band gap values from 2.68 eV to 2.10 eV (ESI, Figure S10).

There have been considerable interest in developing compounds that can exhibit deep ultra-violet cut off due to their application in deep UV optical materials. Many borate and phosphate compounds have been shown to exhibit this property.^[62–65] We made attempts to study the deep-UV cutoff behavior in the newly synthesized $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ (ESI, Figure S11). The $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compound exhibits $\sim 86\%$ of the cut-off at 203 nm, which is one of the best reported UV cut-off values. Similar value is also observed for the parent compound, $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ ($\sim 84\%$), and the Sc^{3+} substituted analogues ($\text{Pb}_2\text{TeFe}_{0.5}\text{Sc}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, and $\text{Pb}_2\text{TeGa}_{0.75}\text{Sc}_{0.25}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\sim 84\%$ at 205 nm. Thus, the burckhardtite compounds may be useful towards deep UV optical windows or deep UV optical prisms.

6. NIR Reflectance Spectra

In the present study, we have prepared new analogue of the burckhardtite compounds and substituted ones. We explored the NIR reflectance behavior of these compounds. The $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compound exhibited a NIR reflectivity of $\sim 65\%$. The Ga^{3+} ions containing $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compound, on the other hand, exhibited a NIR reflectivity of 85%. This value compares well with those reported for the commercial

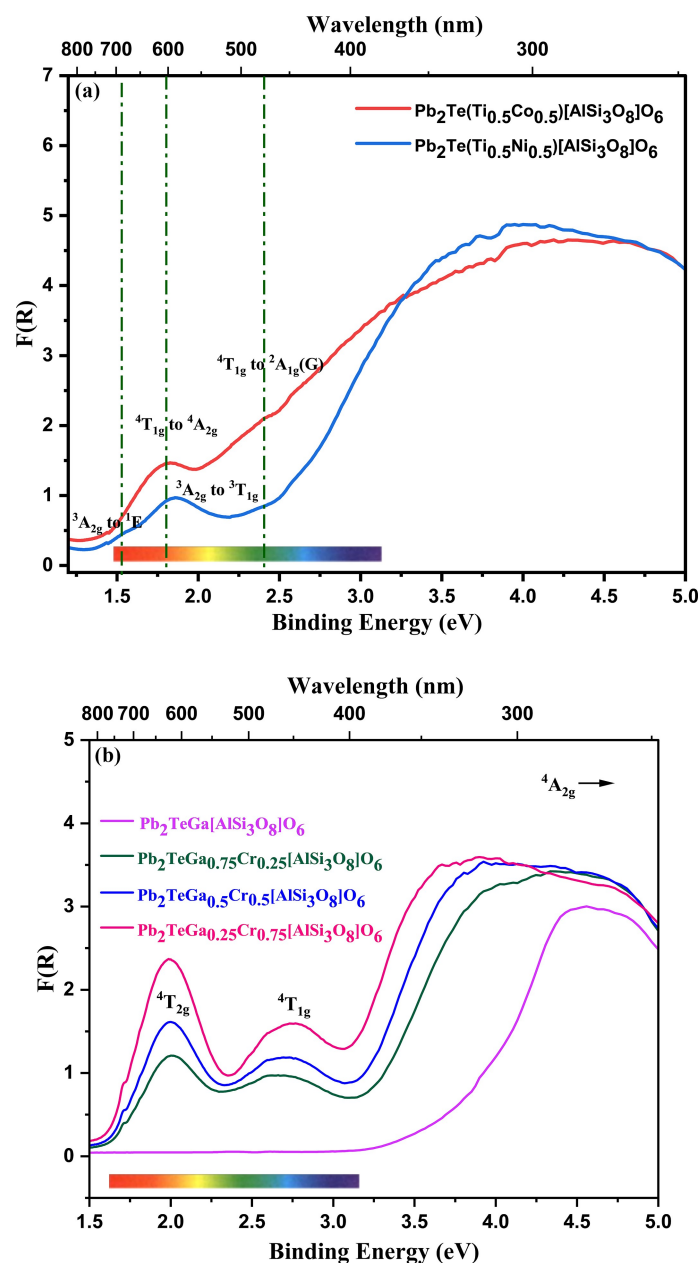


Figure 6. Optical absorption (UV-Vis) spectra of (a) $\text{Pb}_2\text{TeTi}_{0.5}\text{M}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$ (M=Co, Ni), and (b) $\text{Pb}_2\text{TeGa}_{1-x}\text{Cr}_x[\text{AlSi}_3\text{O}_8]\text{O}_6$ ($x = 0.25-0.75$).

NIR reflecting compound, TiO_2 (Figure 7; ESI Figure S12). The Burckhardtite compounds could be good candidates as white pigments with high NIR reflectivity. The Cr^{3+} substituted compounds, $\text{Pb}_2\text{TeFe}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$, and $\text{Pb}_2\text{TeGa}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$ also exhibited reasonable NIR reflectivity of 82% and 74%. Other transition metal substituted compounds typically exhibited lower NIR reflectivity values in the range of $>50\%$. Similar behavior has been observed before.^[42] The colored compounds exhibiting NIR reflectivity of $\sim 50\%$ can be employed as 'cool pigment'.

7. Photoluminescence Studies

The burckhardtite compounds have the Pb^{2+} ions in nine coordination, which might be suitable for investigating lanthanide ion substitution and their luminescence behavior (Figure 8). Thus, we substituted Eu^{3+} ions (1–11%) in the newly prepared $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compound. We substituted Eu^{3+} (1% to 11%) in place of Pb^{2+} in $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$. The excitation spectra of the Eu^{3+} substituted compounds exhibited a number of transitions at 364 nm, 375 nm, 382 nm, 394 nm, and 416 nm which can be assigned to the ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$ transitions.^[66–70] In addition, the excitation spectra also has sharp transitions at 465 nm, 526 nm,

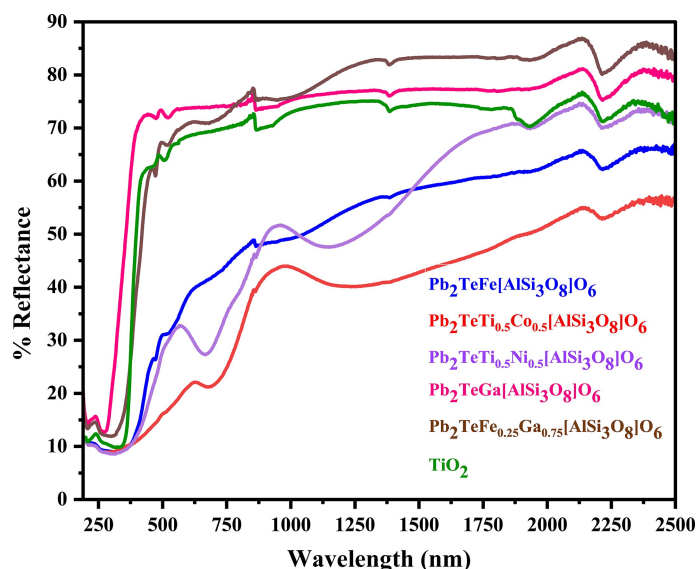


Figure 7. NIR reflectance spectra of $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ and its substituted analogs.

and 534 nm which are due to $^7\text{F}_0 \rightarrow ^5\text{D}_2$, $^7\text{F}_0 \rightarrow ^5\text{D}_1$ and $^7\text{F}_1 \rightarrow ^5\text{D}_1$ transitions, respectively (Figure 8a).^[67,69,71]

We employed an excitation wavelength of 394 nm to probe the emission behavior of $\text{Pb}_{2-x}\text{Eu}_x\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ (Figure 8a). The Eu^{3+} ions exhibited the expected emissions. Thus, we observed emission bands at 578 nm, 591 nm, 612 nm, 646 nm, and 702 nm, which could be assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$, and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively.^[71–73] We found that the emission at 578 nm that corresponds to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ is weaker as it is a forbidden transition ($\Delta J=0$, forced electric-dipole transition) in accordance with Judd-Ofelt's theory.^[74,75] The lack of local symmetry, probably, results in the observation of the forbidden transitions, albeit with weak intensities. As can be noted the emission band at 612 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) has higher intensity compared to that observed at 591 nm (magnetic dipole transition), which suggests that the Eu^{3+} ions occupy positions that have distorted local environment without centre of inversion.^[70] The distortions in the position of Eu^{3+} ions influence the electric dipole transition associated with the $^7\text{F}_2$ energy level of Eu^{3+} .^[70]

As a part of the study, different concentrations of Eu^{3+} ions in $\text{Pb}_{2-x}\text{Eu}_x\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ were synthesized and their emission behavior was investigated. We observed that the emission intensity of the Eu^{3+} ions increases with the increase in the concentration and reaches a maximum value for 9% of Eu^{3+} ions. Higher substitution of Eu^{3+} ions in the compound results in a reduction of the emission intensity, possibly due to the concentration-caused quenching (Figure 8b).

The Fluorescence lifetime was measured for $\text{Pb}_{1.91}\text{Eu}_{0.09}\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ with an emission wavelength of 612 nm and excitation wavelength of 394 nm (Figure 8c). The decay curve is fitted with a tri-exponential function, $I(t) = I_0 + B_1 \left(\exp^{-\frac{t}{\tau_1}} \right) + B_2 \left(\exp^{-\frac{t}{\tau_2}} \right) + B_3 \left(\exp^{-\frac{t}{\tau_3}} \right)$ and the average lifetime is calculated using $\tau_{\text{avg}} = (B_1 \tau_1^2 + B_2 \tau_2^2 + B_3 \tau_3^2) / (B_1 \tau_1 + B_2 \tau_2 + B_3 \tau_3)$ where I and I_0

are the intensities at some t and at $t=0$, B_1 , B_2 and B_3 are the amplitude of decay process and τ_1 , τ_2 and τ_3 are the fluorescence decay times.^[76,77] The average lifetime was calculated to be 0.89 ms for $\text{Pb}_{1.91}\text{Eu}_{0.09}\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$.

8. Dielectric Studies

The Burckhardtite mineral presents an opportunity to investigate the dielectric behavior as such studies have not been carried out. To this end, we have examined the following compounds: $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeFe}_{0.5}\text{Sc}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, and $\text{Pb}_2\text{TeGa}_{0.75}\text{Sc}_{0.25}[\text{AlSi}_3\text{O}_8]\text{O}_6$. The present compounds exhibited higher dielectric constant values at lower frequencies, which decrease on increasing the frequency. This observation is consistent with those normally seen in many oxides (Figure 9).^[78–80] We observed a dielectric constant of 4507 at 1 Hz for the Ga – containing compound, $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ and a value of 1570 at 1 Hz for the Fe compound, $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$. The dielectric constant decreases to 194 at 1000 Hz for the Ga – compound and to 104 at 1000 Hz for the Fe – containing compound. The Sc – substituted compound exhibited the maximum in the dielectric constant value ($\epsilon' = 7756$ at 1 Hz) (Figure 10). All the investigated compounds, however, exhibited low dielectric loss ($\tan \delta$) values.

The dielectric behavior of the compounds is dependent on the different types of polarizations.^[78,79] In addition, lattice distortion, grain boundaries, crystal defects etc may also play a role during the polarization under the applied field. At low applied field, the contributions from all the possible polarization would be affected. At higher frequencies, the ionic, dipolar and space charge polarizations are relaxed out resulting in a lower dielectric constant values.^[81–83] The low dielectric loss, observed in the compounds, indicates that these may be useful in

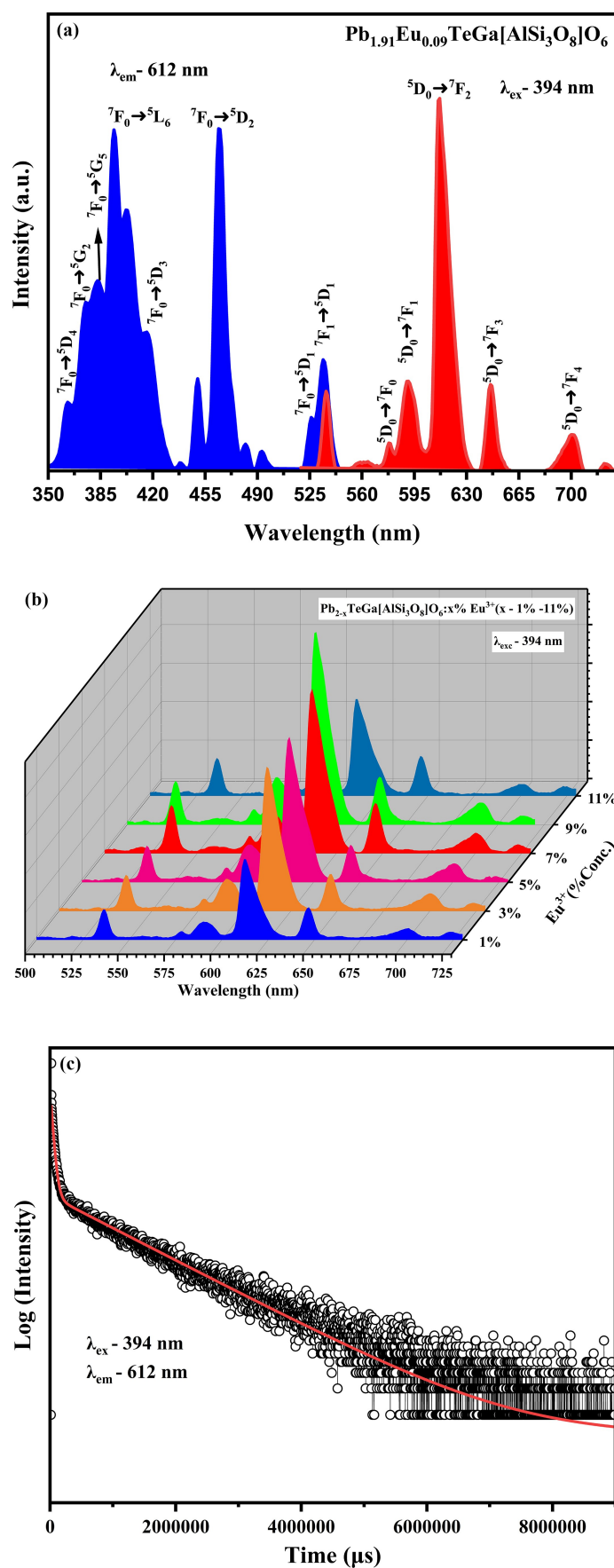


Figure 8. PL and PLE spectra of (a) $\text{Pb}_{1.91}\text{Eu}_{0.09}\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ (b) PL spectra of $\text{Pb}_{2-x}\text{Eu}_x\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ ($x = 0.01$ – 0.11), and (c) Decay curve of $\text{Pb}_{1.91}\text{Eu}_{0.09}\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$ monitored at 612 nm.

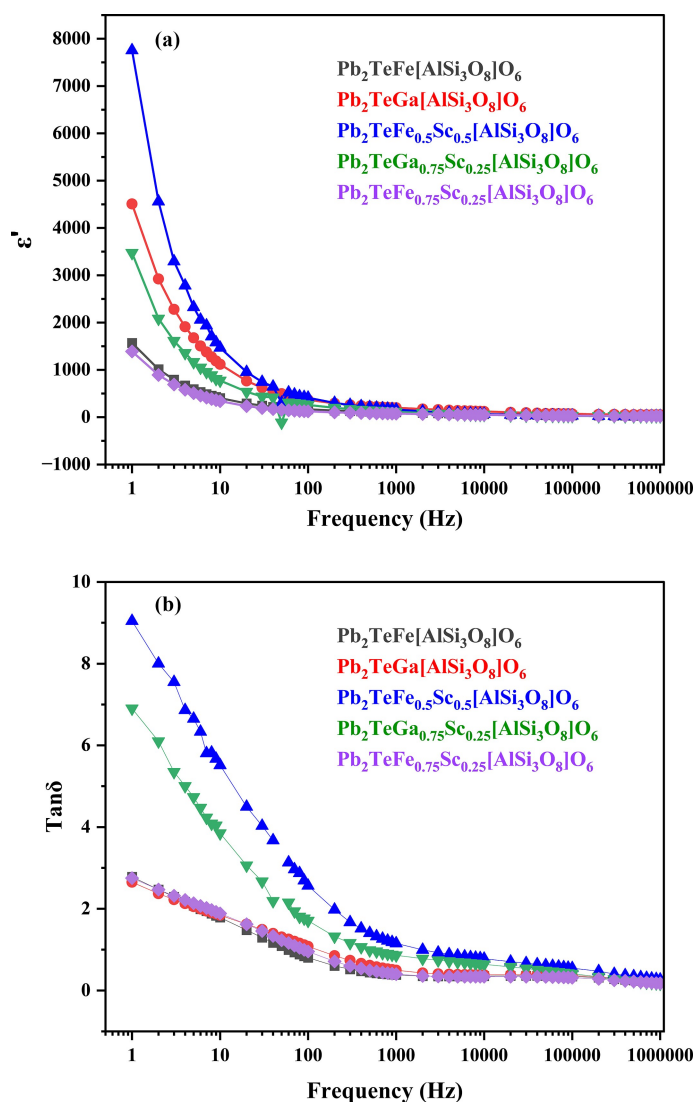


Figure 9. (a) The relative dielectric constant trend of the synthesized compounds, $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeFe}_{1-x}\text{Sc}_x[\text{AlSi}_3\text{O}_8]\text{O}_6$ ($x = 0.25, 0.5$), and $\text{Pb}_2\text{TeGa}_{0.75}\text{Sc}_{0.25}[\text{AlSi}_3\text{O}_8]\text{O}_6$ (b) The dielectric loss ($\tan\delta$) trend of $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeGa}[\text{AlSi}_3\text{O}_8]\text{O}_6$, $\text{Pb}_2\text{TeFe}_{1-x}\text{Sc}_x[\text{AlSi}_3\text{O}_8]\text{O}_6$ ($x = 0.25, 0.5$), and $\text{Pb}_2\text{TeGa}_{0.75}\text{Sc}_{0.25}[\text{AlSi}_3\text{O}_8]\text{O}_6$.

communication devices, especially at higher operating frequencies.^[84]

9. Magnetic Studies

The magnetic behavior of the compounds were also investigated as a function of temperature (Figure 10; ESI, Figure S13). The room temperature magnetic susceptibility value of the parent compound, $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$ was found to increase as a function of temperature (Figure 10a).^[82] The $\chi_m - T$ value exhibits a sharp rise below 50 K to reach a maximum value of $0.26 \text{ emu mol}^{-1}$. The $1/\chi_m - T$ was fitted to a Curie-Weiss behavior in the temperature range of 100–300 K, which gave values for θ of -7.56 K , and C of $4.45 \text{ emu mol}^{-1} \text{ K}$. The small negative θ value suggests antiferromagnetic interactions. The effective magnetic moment for the compound at 300 K was

calculated to be $5.89 \mu_B$ which is in agreement with the spin-only values for the Fe^{3+} ($5.91 \mu_B$, $3d^5$, $s = 5/2$). The M vs H plot at 2 K and 300 K was found to be in the expected manner for a compound possessing antiferromagnetic interactions (ESI, Figure S13).

The magnetic susceptibility studies of the $(\text{Ti}_{0.5}\text{Co}_{0.5})$ containing compound, $\text{Pb}_2\text{TeTi}_{0.5}\text{Co}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$, also exhibits a behavior similar to the Fe^{3+} – containing compound. The $\chi_m - T$ values slowly increases and exhibits a sharp rise at $\sim 25 \text{ K}$. A maximum molar magnetic susceptibility of $0.21 \text{ emu mol}^{-1}$ was observed at 2 K (Figure 10b). The $1/\chi_m - T$ data fitted in the temperature range of 50–300 K, which gave a value of $\theta = -89.01 \text{ K}$, and $C = 1.99 \text{ emu mol}^{-1} \text{ K}$. The calculated effective magnetic moment for the $\text{Pb}_2\text{TeTi}_{0.5}\text{Co}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$ compound was found to be $3.79 \mu_B$, which matches well with the spin only value of Co^{2+} ions ($3.87 \mu_B$, $3d^7$, $s = 3/2$). We also observed that there exists a small divergence between ZFC and FC at 5–15 K

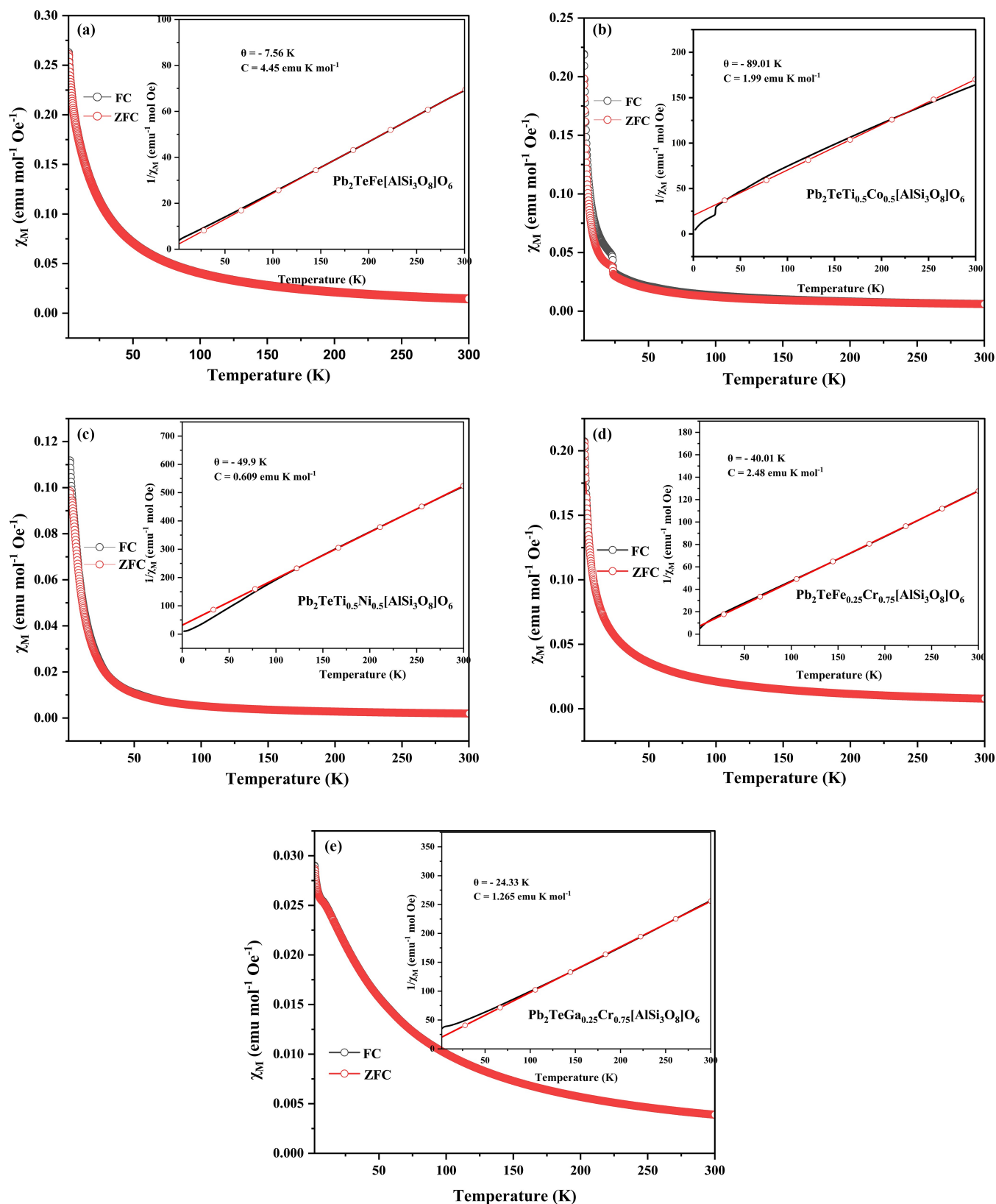


Figure 10. Magnetic studies (χ_M vs T) for, (a) $\text{Pb}_2\text{TeFe}[\text{AlSi}_3\text{O}_8]\text{O}_6$; (b) $\text{Pb}_2\text{TeTi}_{0.5}\text{Co}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$; (c) $\text{Pb}_2\text{TeTi}_{0.5}\text{Ni}_{0.5}[\text{AlSi}_3\text{O}_8]\text{O}_6$; (d) $\text{Pb}_2\text{TeFe}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$ and (e) $\text{Pb}_2\text{TeGa}_{0.25}\text{Cr}_{0.75}[\text{AlSi}_3\text{O}_8]\text{O}_6$. (Inset of the figure shows $1/\chi_M$ vs T for all the samples)

which may be due to the interactions between the magnetic ions. The FC magnetization exhibited values that are larger than the ZFC values. It is likely that the magnetic interactions are stronger at low temperatures, which may lead to ordering. The other possibility is that the ZFC state may be frozen or disordered due to the competing interactions or slow relaxation. From the M–H plot at 2 K, one can observe that there could be weak ferromagnetic interactions due to the spin canting within an overall antiferromagnetic system. This behavior could give rise to a small net magnetization, which saturates at higher fields. A similar behavior was also observed for the (Ti_{0.5}Ni_{0.5}) containing compound, Pb₂TeTi_{0.5}Ni_{0.5}[AlSi₃O₈]O₆ as well (Figure 10c; ESI Figure S13).

We also compared the magnetic properties of Cr³⁺ ions containing compounds, Pb₂TeFe_{0.25}Cr_{0.75}[AlSi₃O₈]O₆ and Pb₂TeGa_{0.25}Cr_{0.75}[AlSi₃O₈]O₆ (Figure 10d and 10e). The maximum molar magnetic susceptibility values were observed at 2 K of 0.21 emu mol^{−1} and 0.03 emu mol^{−1} for Pb₂TeFe_{0.25}Cr_{0.75}[AlSi₃O₈]O₆ and Pb₂TeGa_{0.25}Cr_{0.75}[AlSi₃O₈]O₆, respectively. The 1/χ_m – T data was fitted in the temperature range of 100 K–300 K for Pb₂TeFe_{0.25}Cr_{0.75}[AlSi₃O₈]O₆, which gave the values of θ = −40.01 K, and C = 2.48 emu mol^{−1} K, respectively. However, the Curie-Weiss fit for Pb₂TeGa_{0.25}Cr_{0.75}[AlSi₃O₈]O₆ gave values of θ as −24.33 K, and C as 1.265 emu mol^{−1} K. This may be expected as there may be interaction between Fe³⁺ (d⁵) ions and Cr³⁺ (d³) ions, which could have enhanced the anti ferromagnetic interactions. The calculated effective magnetic moment at 300 K for Pb₂TeFe_{0.25}Cr_{0.75}[AlSi₃O₈]O₆ was found to be 4.3 μ_B, which is slightly higher than that observed for Pb₂TeGa_{0.25}Cr_{0.75}[AlSi₃O₈]O₆ (3.05 μ_B). The spin only value for Cr³⁺ ions is 3.87 μ_B (s = 3/2). The small hump at ~10 K with overlapping ZFC and FC indicates that, it could be the onset of long-range ordering in the compound.

10. Conclusions

A new synthetic analogue, Pb₂TeGa[AlSi₃O₈]O₆, of the naturally occurring mineral, Burckhardtite – Pb₂TeGa[AlSi₃O₈]O₆, has been successfully synthesized under laboratory conditions employing solid state technique. The substitution of transition elements in place of Ga by a combination of Ti_{0.5}M_{0.5} (M = Co, Ni) resulted in phase-pure compounds exhibiting different shades of green. The partial substitution of Mn³⁺ and Cr³⁺ in place of Ga/Fe in the compounds also resulted in pink and green colored compounds. The white colored, Pb₂TeGa[AlSi₃O₈]O₆ compound exhibited good NIR reflectivity. The Cr³⁺ substituted green compounds also showed good NIR reflectivity, which may be beneficial towards developing ‘cool pigments’. The Eu³⁺ ions substituted compounds exhibit good red – luminescence. The reasonably good dielectric values with low dielectric loss would prompt the utility of these compounds in communication devices. The Ga-compound exhibited a good deep UV-cut off behavior, which may of use in deep UV optical prism and deep UV optical windows. The magnetic studies indicate anti-ferromagnetic behavior. The present study illustrates that it is

possible to prepare synthetic analogue of the naturally occurring mineral Burckhardtite. This provides impetus to explore the synthesis of other minerals and investigating them towards new material properties. We are presently pursuing this theme actively.

Experimental Section

All the compounds were synthesized by conventional solid-state technique. Stoichiometric mixtures of the starting materials were carefully weighed and ground in a mortar and pestle for 30 minutes, transferred onto a alumina crucible, and heated in air at 780–840 °C for varying time periods with intermittent grindings (Table S1). The products were analyzed for their phase purity using PXRD.

The PXRD patterns were recorded employing Philips X'pert Diffractometer (Ni filtered Cu Kα radiation, λ = 1.5418 Å). (Figure 1; ESI Figure S1) The newly synthesized compound, Pb₂TeGa[AlSi₃O₈]O₆, was refined using the Rietveld refinement. For this, the PXRD data were collected at room temperature in the 2θ range of 5–120° with a step size of 0.02° and a step duration of 50s. The PXRD pattern was refined by GSAS-EXPGUI.[85] Lattice parameters, scale factor, background (Fourier polynomial background function), pseudo-Voigt (U, V, W, and X), and isothermal parameter (U_{iso}) were refined. Thermal parameters were constrained to be the same for different atoms occupying the same site. The optical studies were carried out on powdered samples employing a Perkin-Elmer Lambda 950 UV-Vis double-beam spectrometer in the spectral region of 200–2500 nm (Figure 4). The diffuse reflectance data were converted to the Kubelka–Munk.^[86]

$$F(R) = (1 - R)^2 / 2R = \alpha / S$$

in which R is the reflectance, α is the absorptivity, and S is the scattering factor. The optical band gap was calculated by Tauc plot,^[87] using the function

$$\alpha h\nu = A [h\nu - E_g]^n$$

Where α is the absorption coefficient, A is known as the band tailing parameter and n is the power factor of the transition mode. The plot of (αhν)^{1/n} versus the photon energy (hν) was extrapolated to give the value of band gap (E_g).

The dielectric measurements were carried out using a NoVo control impedance analyzer (Alpha-A) in the frequency range of 0.1 Hz–1 MHz. Micro-Raman spectra were recorded at room temperature using a triple monochromator DXR microscope Raman spectrometer, equipped with 1800 groove/mm diffraction grating and a liquid nitrogen-cooled CCD detector. 10 mW output of 532 nm line of Nd:YAG (10 mW) was used as the excitation source.

The Magnetic measurements were carried out in the temperature range 2–390 K employing a SQUID Magnetometer under an applied field of 1000 oe.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Burckhardtite mineral · High dielectric constant material · Red Photoluminescence · Anti ferromagnetism · Deep UV Cutoff material · Metal-to-metal charge transfer

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